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(54) QUATERNARY AMMONIUM DERIVATIVES OF EPICHLOROHYDRIN POLYMERS

(71) We, THE FIRESTONE TIRE & RUBBER COMPANY, a Corporation organized under the laws of the State of Ohio, United States of America, of 1200 Firestone Parkway, Akron, State of Ohio, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a quaternary ammonium derivative of high molecular weight epichlorohydrin polymers and copolymers, and the process of flocculating suspensions therewith.

The prior art discloses polyquaternary ammonium salts of polyepichlorohydrin of relatively low molecular weight. Thus Walker et al U.S. Patent No. 3,428,680 shows an epichlorohydrin homopolymer of relatively low molecular weight in which a portion of the repeating units bearing the chlorine atom have been reacted with a tertiary amine to produce a quaternary ammonium derivative repeating unit. From the fact that the combined number of repeating units in the polymer is no greater than 50 and from the size of the alkyl groups defined for the repeating units, it is calculated that the molecular weight has a maximum of about 25,000. These particular derivatives are used for antibacterial purposes.

Rogers et al U.S. Patent No. 3,320,317 discloses the quaternization of epichlorohydrin homopolymers having a relatively low molecular weight as evidenced by the fact that in Column 1, Lines 30—35, the number of epichlorohydrin repeating units is defined as from 4 to about 500. Since this repeating unit is equivalent to a molecular weight of 93, a polymer having 500 of these repeating units would have a molecular weight of about 46,500.

In the paragraph bridging Columns 3 and 4, the patentees state, "Alternatively, particularly for the higher molecular weight polyepichlorohydrins, it is sometimes desirable to dissolve the polyepichlorohydrins in a minimum amount of water miscible organic solvent such as dioxane or alcohol and to add the resulting solution to an aqueous or alcoholic solution of the trialkylamine reactant. The use of a reaction solvent appears to be necessary for accomplishing a desirable degree of substitution of quaternary groups on the polymer, since attempts to react the polyepichlorohydrin with trialkylamines under anhydrous or substantially anhydrous conditions produces a product having an insufficient content of quaternary ammonium groups to render the same water-soluble."

From this it is obvious that higher molecular weight polyepichlorohydrins, even in the low range specified, presented difficulties in solubility and reaction. Consequently, higher molecular weights of the polyepichlorohydrins were avoided. In fact, the molecular weight of the polyepichlorohydrins in the various examples are in the range of 500—1,500.

There are various disadvantages in a polyepichlorohydrin of low molecular weight, particular where not all of the chlorine has been displaced by the quaternary ammonium group. The presence of the covalent chlorine renders the product less water soluble and may contribute other disadvantages in the presence of aminoacids and other reactive materials in the effluent liquids being flocculated.

In accordance with the present invention it has been found that polyquaternary ammonium derivatives of polyepichlorohydrins where the derivatives have a much higher molecular weight, that is at least 150,000 and preferably at least 200,000, are much more effective in a flocculating process, and an improved polyquaternary ammonium composition can be prepared by starting with a copolymer of epichlorohydrin and an alkylene oxide, preferably ethylene oxide, but also propylene oxide, butylene oxide, amylene oxide, etc. The

starting copolymer advantageously has 5—75, preferably 15—50 mole percent of epichlorohydrin and 25—95, preferably 50—85 mole percent of the alkylene oxide therein. Advantageously the copolymer has approximately the same number of epichlorohydrin repeating units as the number of quaternary ammonium repeating units desired in the ultimate polymer. Then by substantially completely replacing the covalent chlorine, which is present in lower amount and is more spaced in the copolymers than in the homopolymers, by quaternary ammonium groups the resultant quaternized polymer is substantially free of covalently bonded chlorine. Furthermore, complete replacement of the covalently bonded chlorine makes more effective and complete use of the more expensive epichlorohydrin component.

The presence of the alkylene oxide repeating unit has a number of advantages including the speeding up of the reaction, possibly due to the spacing of the epichlorohydrin radicals from each other, and improved solubility due to the alkylene oxide groups. Moreover, the resultant copolymer has the quaternary ammonium groups similarly distributed and spaced throughout the polymer so that they can be more effectively used in the flocculation process.

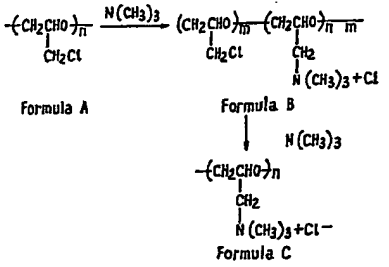
Moreover, the alkylene oxide radicals improve the water solubility of the starting copolymer and avoid the disadvantages of insolubility as quoted above from one of the prior art patents. In this way much higher molecular weight polymers can be used in the quaternization reaction without difficulty and the much higher molecular weight polyquaternary ammonium polymer is more effective in the flocculation process.

Reference herein to molecular weight is to number average molecular weight determined by the well known osmotic pressure method specifically the dynamic method of applying osmodic pressure. This method is described in numerous publications such as "Organic Chemistry of Macromolecules—An Introductory Text book" by A. Ravve (1967), chapter 3, pages 43—44, published by Maxel Dekker, Inc. New York.

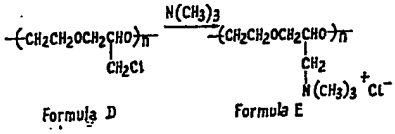
Epichlorohydrin polymers suitable for the practice of this invention can be prepared according to methods disclosed in the literature, for example pp. 196—202 on "Epichlorohydrin Elastomers" in Encyclopedia of Polymer Science and Technology, Vol. 6 (1967), Interscience Publishers, New York; Hydrin Elastomers Bulletin, Sections 1—9, B.F. Goodrich Chemical Co., Cleveland, Oct. 1965; W. R. Leach, Paper, Amer. Chem. Soc., Div. Rubber Chem. Meeting, Philadelphia, Pa., Oct. 1965; and W. D. Willis et al, Paper, Amer. Chem. Soc., Div. Rubber Chem. Meeting, Philadelphia, Pa., Oct. 1965.

While the quaternary ammonium derivatives of high molecular weight polyepichlorohydrin are more effective as flocculating agents than the corresponding low molecular weight materials of the prior art, the corresponding derivatives of the high molecular weight copolymers of epichlorohydrin and alkylene oxides are even much more effective, and are therefore preferred as flocculating agents even in comparison with the high molecular weight derivatives of the homopolymers.

The polyepichlorohydrin polymer structure has the repeating unit structure shown in Formula A and upon reaction with trimethyl amine has the intermediate structure of Formula B and upon complete conversion has the structure of Formula C.

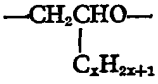


In contrast the ethylene oxide-epichlorohydrin copolymer has the respective epichloorhydrin repeating units or their quaternary ammonium derivative spaced from each other and separated by ethylene oxide repeating units as illustrated below for a copolymer having 50 mole percent each of ethylene oxide and epichlorohydrin or the corresponding quaternary ammonium derivative:



Formula E shows the copolymer completely converted to the ammonium derivative, which form is more quickly and easily attained with the ethylene oxide copolymer than with the epichlorohydrin homopolymer. Moreover with higher or lower mole percent of the ethylene oxide or other alkylene oxide, the frequency of recurrence of the corresponding repeating unit will vary accordingly.

The alkylene oxide repeating unit can be represented as



wherein x is zero or an integer of 1, 2, etc. For water solubility purposes, x is advantageously no greater than 4.

Tertiary amines preferred for the quaternization are trimethyl amine and pyridine. Tetramethyl ethylenediamine and N,N-dimethyl piperazine can also be used for quaternization but since they are difunctional they act also as chain extenders. This is beneficial when the starting polymer is of a relatively low molecular weight. Generally, however, these difunctional amines are used in conjunction with trimethyl amine or pyridine, preferably about 0.1—0.2% based on the weight of the trimethyl amine or pyridine.

Apparently the less hindered approach to the nitrogen made possible by the small methyl group and by the structure of the pyridine make these amines more easily and quickly reactive.

Although the number of chlorine atoms per polymer molecule in the starting polymer and in the quaternized ammonium polymer is the same in view of the fact that the covalently bonded chlorine is converted to ionic chlorine, the interposing of the $-N(CH_3)_3^+$ or other quaternary ammonium radicals increases the proportion of non-chlorine matter in the polymer molecule and thereby reduces the percent by weight of chlorine.

The trimethyl amine reaction is advantageously effected at 60—120° C., preferably about 80—110° C. Below 60° C. the reaction is so slow as to be impractical. At temperatures above 120° C., the polymers have a tendency to degrade. With pyridine the reaction occurs at 0—80° C. and preferably at 20—60° C. Polymer degradation occurs at temperatures above 80° C.

The tertiary amine is used advantageously in a proportion of 1—8 moles of amine per atom of chlorine to be reacted, with 2.5—4 moles of amine per chlorine atom generally being preferred. The amine is advantageously added as an aqueous solution, generally 10—30%, or preferably 25% by weight concentration.

The reaction is conducted in a pressure reactor with stirring under autogenous pressure. The time of completion of the reaction is in the range of two to 24 hours depending on the temperature and the concentration of reagents.

After the reaction has been completed the excess amine is removed by vaporization. This removal can be effected by gradual evacuation or by introduction of the reaction product solution into a flash vaporizer. The product is advantageously retained in solution and used as such. If it is recovered in solid form, it becomes brittle and loses its solubility upon drying. The solid is white and hygroscopic. If the dried, brittle solid is heated about 100° C., water is driven off and the polymer is degraded and made water soluble again.

As previously indicated, these quaternary ammonium polymers are particularly useful for flocculation of suspensions, such as elutriated sewerage, various other wastes such as mining and ore waste liquids, for hydrodynamic acceleration, lubricant compositions, water soluble packaging compositions, etc., and can be used for making potable water out of lake and river water. Preferably, the polymer is added in the form of an aqueous solution in a quantity to give 0.05 to 0.4 parts of polymer per 100 parts of solid particles in suspension. For such purposes we have found that flocculation is more efficient with increased molecular weight of the polymer. Advantageously the molecular weight of the starting epichlorohydrin polymer is at least 150,000, and preferably at least 200,000, and favorably as high as conveniently obtainable. Also as previously indicated, the ethylene or other alkylene oxide copolymers are preferred particularly for improved water solubility of the copolymer and for more effective use of the more expensive epichlorohydrin component.

An elutriated sewerage sludge having 6.9% solids and no flocculent requires about 19 minutes filtration to give a filter cake of 70% water, which is a product that can be handled and burned easily. With the polymers of this invention it is possible to produce a product having the water content reduced to 70% within 1.8 minutes; to 65% in 3.5 minutes; and to 60% in 8.3 minutes. If these polymers are used on very dilute sewerage as it comes into the sewerage plant, it is possible to eliminate settling tanks.

Various methods of practicing the invention are illustrated by the following examples. These examples are intended merely to illustrate the invention and not in any sence to limit the manner in which the invention may be practiced. The parts and percentages recited therein and all through the specification, unless specifically provided otherwise, are by weight.

Example I.

Into a pressure reactor equipped with stirrer, there is introduced 100 g. of an ethylene oxide-epichlorohydrin copolymer having 50 mole percent of ethylene oxide and a molecular weight of 300,000, and 740 ml. of 25% trimethyl amine aqueous solution. This provides a mole ratio of amine to chlorine of 4 to 1. Reaction is conducted at 100° C. for 6 hours under autogenous pressure, which reaches a maximum of 34 psi. The original copolymer has a chlorine content of 26%, and after reaction the produce has a chlorine content of 18.2% due to the increase in copolymer weight by the quaternization. The resulting solution is admitted gradually to a flash evaporator or a vessel maintained under vacuum to vaporize the unreacted amine.

Water is added periodically to replace the water that is removed by distillation with the amine. Sufficient water is added to give the fluidity necessary to permit stirring. The evaporation is continued until unreacted amine has been completely removed. The product is maintained in solution during the amine removal and is recovered as a solution for ultimate use.

EXAMPLE II.

The procedure of Example 1 is repeated using in place of the copolymer, a homopolymer of epichlorohydrin of approximately the same molecular weight, and using 685 ml. of 25% trimethyl amine aqueous solution. This gives a ratio of 2.5 moles of amine per atom of chlorine, which has been found to be a convenient ratio to effect reaction. The reaction is completed in 8 hours at 100° C. The starting homopolymer has a chlorine content of 38.4% and the quaternized product has 23.4% chlorine. The product solution is processed as in Example I to remove unreacted amine.

EXAMPLE III.

The procedure of Example I is used in preparing a polyquaternary ammonium derivative of the same copolymer using a temperature of 80° C. and carrying out the reaction in one case (a) for 8 hours, and in another case (b) for 20 hours. These two products, IIa and IIb, are tested as flocculants in an elutriated sewerage sludge having 6.9% solids. A control test is also run using no flocculent. In each case after the aqueous solution of the flocculating agent is added, filtration is effected on an 11 cm. Buchner funnel under a vacuum of 20 inches of mercury. The time in minutes is noted for removal of sufficient water from the sludge to form a tight cake. Such a cake generally contains 68—72% moisture. The time required to remove water to 70% moisture is estimated from curves plotted from related data. The results are given below in Table I.

TABLE I

Flocculating Agent	% Based on Sludge Solids	Filtration Time (Mins)	% Moisture in Filter Cake	Mins. to 70% Moisture
None	0.0	20	67	18.8
IIa	0.2	1.5	73	2.5
"	"	6.5	62	—
"	"	20	59	—
IIb	0.2	1.5	71	1.8
"	"	6.5	61	—

EXAMPLE IV.

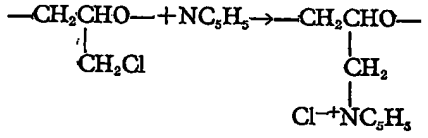
The procedure of Example III is repeated in four tests to compare polyquaternary ammonium derivatives of epichlorohydrin homopolymers and ethylene oxide copolymers. The homopolymer derivatives are prepared according to Example II and the copolymer derivatives according to Example I. The results are given in Table II.

TABLE II

Flocculating Agent	Mol. Wt. Epichlorohydrin Polymer	% Based on Sludge Solids	Filtration Time (Mins.)	% Moisture in Filter Cake	Mins. to to Moisture
Homopolymer A	150,000	0.1	2.25	72	2.9
Homopolymer B	275,000	0.1	2.0	72	2.7
Copolymer C	300,000	0.1	2.0	68	1.5
Copolymer D	226,000	0.1	2.0	70	2.0

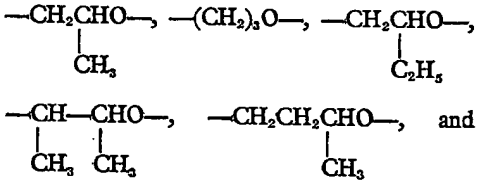
EXAMPLE V.

Similar improvements are noted when the procedures of Examples I—IV are repeated using equivalent amounts of pyridine in place of the trimethyl amine. The polymeric repeating unit structure can be represented as follows:

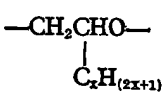


EXAMPLE VI.

Improved results are also obtained when the procedures of Examples I, III and IV are repeated using corresponding copolymers 1,2-propylene oxide, 1,3-propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, 1,3-butylene oxide and 1,4-butylene oxide (tetrahydrofuran) in place of the ethylene oxide. The corresponding repeating units are



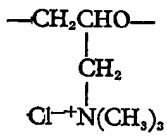
—$(CH_2)_4O$—. These are considered equivalent to —CH_2CH_2O— for the purposes of the invention and are therefore considered as encompassed by the scope of the generic repeating unit of



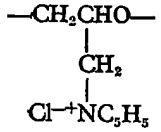
WHAT WE CLAIM IS:—

1. A quaternary ammonium polymer composition having a molecular weight of at least 150,000 and having in the polymer chain thereof a plurality of quaternary ammonium repeating units, said polymer compositions being the reaction product of a tertiary amine and a polyepichlorohydrin, said polyepichlorohydrin being a homopolymer of epichlorohydrin or a copolymer of epichlorohydrin and an alkylene oxide.

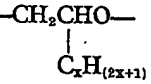
2. A quaternary ammonium polymer composition having a molecular weight of at least 150,000 and having in the polymer chain thereof a plurality of quaternary ammonium repeating units having at least one of the formulas selected from the class consisting of:



and



3. The polymer composition according to claim 2, in which the polymer also has a plurality of alkylene oxide repeating units therein having the formula



wherein x is zero an integer having a value of 1—4.

4. A composition according to claim 3, in which the polymer has 25—95 of the alkylene oxide repeating units and 5%75 of the quaternary ammonium repeating units per 100 repeating units of said polymer.

5. A polymer composition of claim 3, in which the polymer has 50—85 of the alkylene oxide repeating units and 15—50 of the quaternary ammonium repeating units per 100 repeating units of said polymer.

6. A composition according to claim 4 or 5, in which the alkylene oxide repeating units have the formula

$$—CH_2CH_2O—$$

7. A quaternary ammonium polymer composition substantially as hereinbefore described with reference to the Examples .

8. A process of flocculating solid particles from an aqueous suspension thereof comprising intimately mixing therewith an aqueous solution of the polymer composition of any one of the preceding claims.

9. A process according to claim 8, in which the polymer aqueous solution is added in a quantity to give 0.05—0.4 parts of polymer per 100 parts of solid particles in the suspension.

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